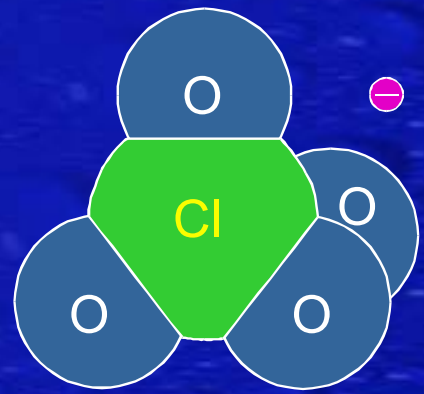
Perchlorate by Ion Chromatographic Methods:
A Methods Development Status Report

Department of Defense
IDQTF-EDQW Round Table

October 23, 2003
Dallas, TX



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Presentation Outline

- Current Status of Method 314.0 using improved RFIC Instrumentation and Ultra II Suppressor
- Sample Pretreatment for Matrix Removal and Detection Limit Enhancement
- Automated Sample Preconcentration for Matrix Removal and Lowering Detection Limits
- Second Column Confirmation with the Cryptand A1 Column
- IC-MS Detection for Low Parts-per-Trillion Determinations

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Review of EPA Method 314.0 for Perchlorate
Revision 1.0, November 1999

- Analytical method: ion chromatography with suppressed conductivity detection
- Key operating conditions

Column:	IonPac® AG16, AS16, 4-mm
Eluent:	50 mM sodium hydroxide
Flow Rate:	1.5 mL/min
Suppressor:	ASRS® ULTRA, external water mode
Sample Loop:	1,000 µL

- Method must deliver adequate column efficiency (peak area/height ratio – A/H) to allow quantification at the required MDL in a sample with high total dissolved solids (TDS)
- Must be able to quantify in a test matrix of chloride, carbonate, and sulfate at 600 mg/L each (TDS_{600})

DIONEX

ICS-2000 Integrated RFIC System

- Integral eluent generation
- Dual-piston pump with optional vacuum degas
- Electrically actuated injection valve
- Column heater, (30–60 °C)
- Electrolytic suppressor control
- Thermally controlled conductivity detector (±0.01 °C)
- LCD touch-pad front panel

DIONEX

Reagent-Free IC

SRS® ULTRA II Design Changes

SRS ULTRA II Design Change	Feature	Advantage	Benefit
Solvent cleaned screens and membranes	Less leachates	Lower background Lower noise Faster start-up	Increased sensitivity Better detection limits Better integration for early eluting anions Time savings
New proprietary gasket material	Less leachates	Lower background Lower noise Faster start-up	Increased sensitivity Better detection limits Better integration for early eluting anions Time savings
Screen capacity increased	Lower voltage (ASRS®)	Less prone to fouling	Uninterrupted operation

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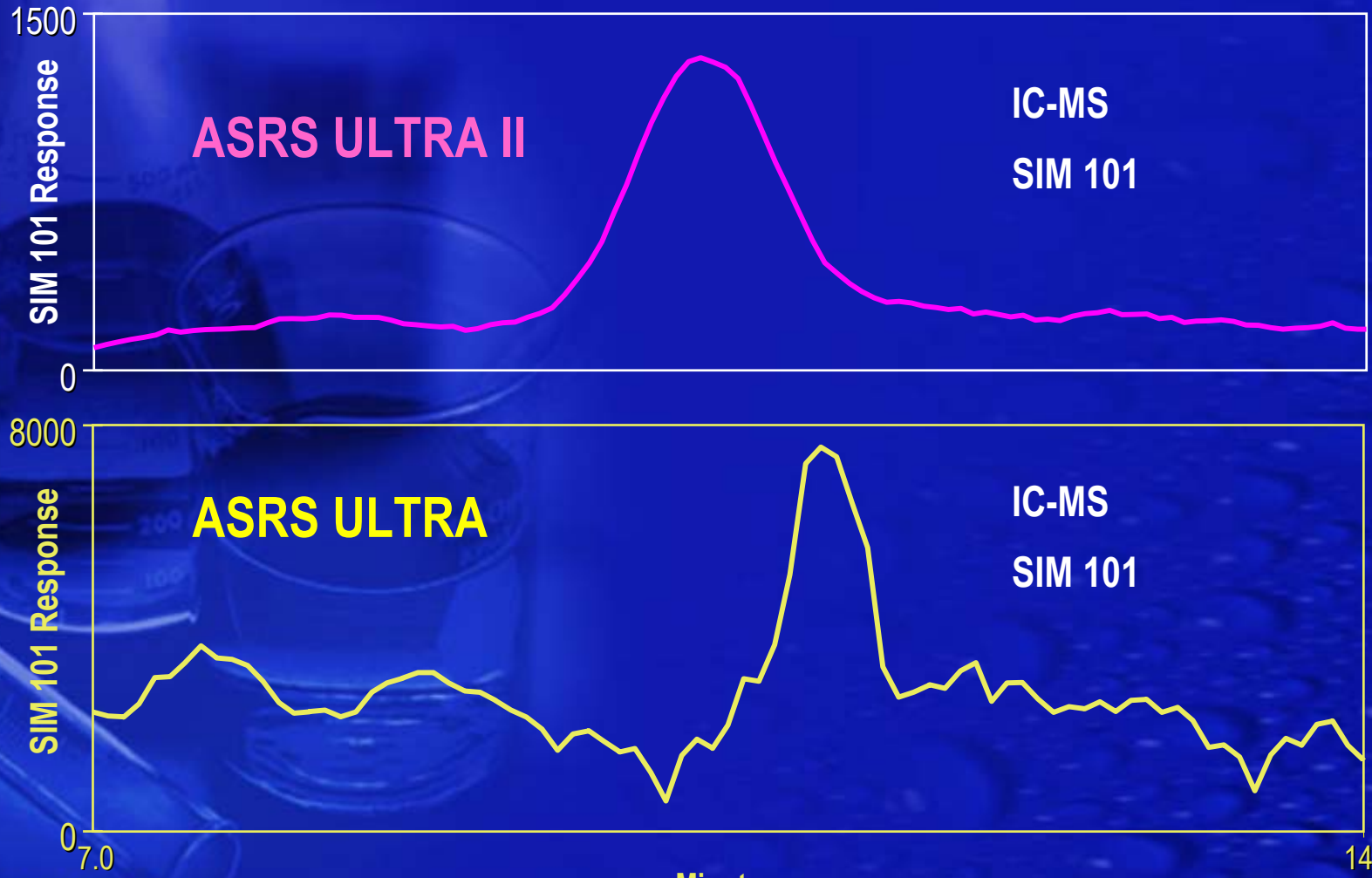
ASRS® ULTRA and ULTRA II Comparison

Perchlorate IC-MS Method



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SRS® ULTRA II Performance Characteristics

- Fast start-up times
  - <2 hours for both 2– and 4-mm anion and cation applications upon first install
  - Day to day start-up is <5 min
- Hydroxide eluent applications typical noise in recycle mode
  - <1 nS/cm up to 40 mM NaOH
  - <2 nS/cm up to 100 mM NaOH
  - External water recommended for trace applications
- Low void volume improves efficiency for early-eluting peaks for anions

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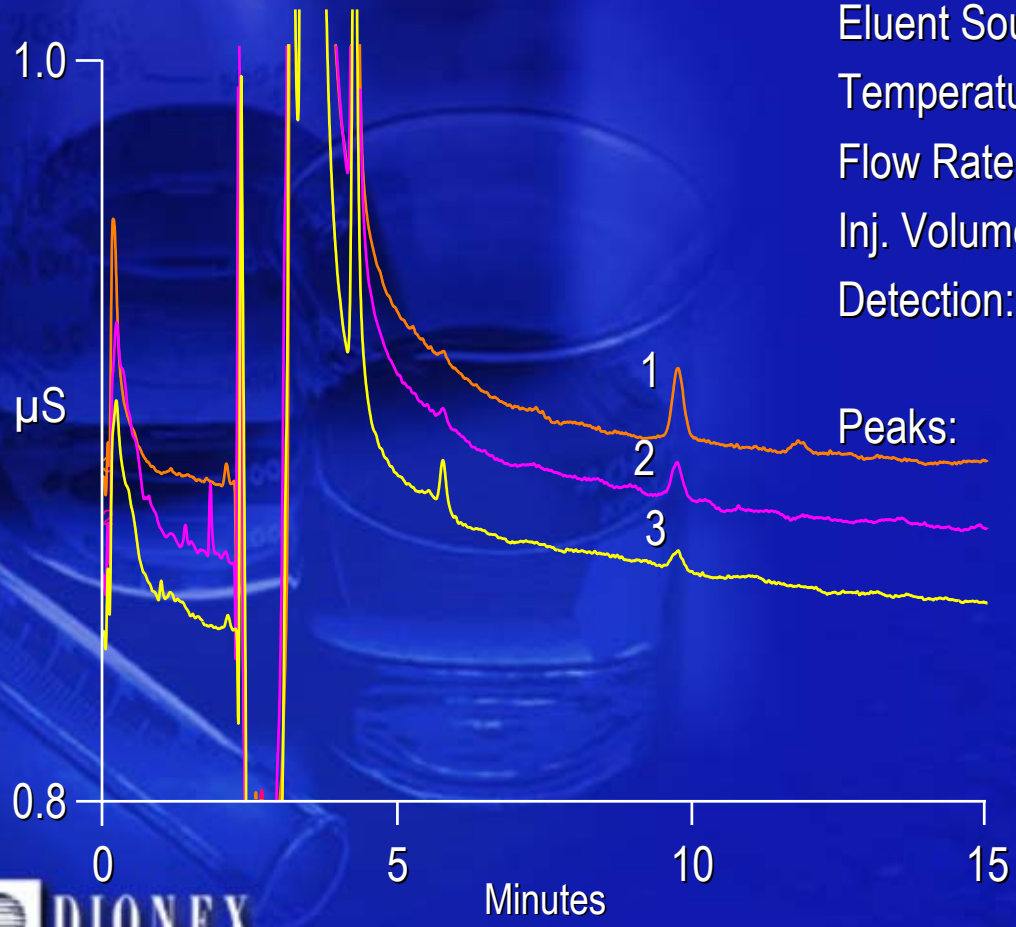
Trace-Level Perchlorate Using the ASRS® ULTRA II
ICS-2000



Column:	IonPac® AG16, AS16 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 with EGC and CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Inj. Volume:	1000 µL
Detection:	ASRS ULTRA II, recycle mode

Peaks:

1. Perchlorate 2.0 µg/L (ppb)
2. Perchlorate 1.0
3. Perchlorate 0.5

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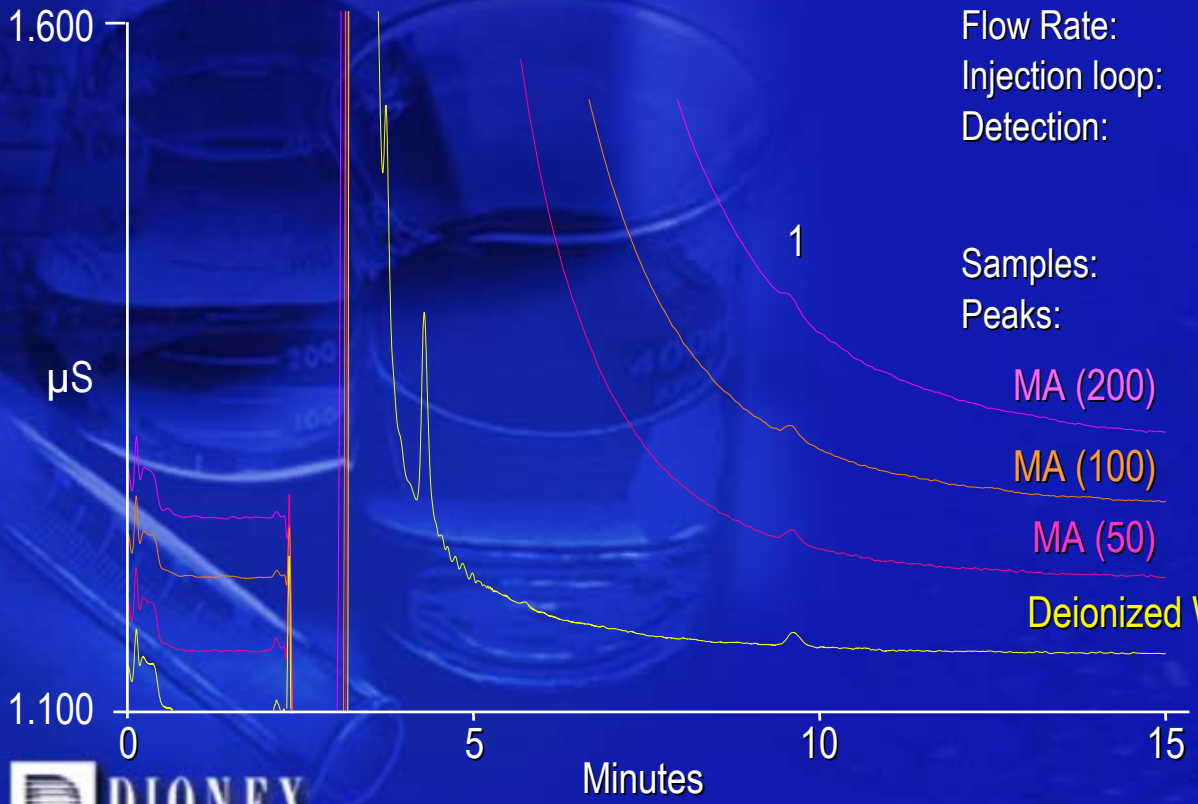
19339

EPA Method 314.0

Determination of 1 µg/L Perchlorate with Increasing Concentrations of Chloride, Sulfate, and Carbonate



Column:	IonPac® AG16, AS16, 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 EG with CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Injection loop:	1000 µL
Detection:	ASRS® ULTRA II, AutoSuppression®, external water mode, 193 mA
Samples:	MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}
Peaks:	1. Perchlorate 1 µg/L

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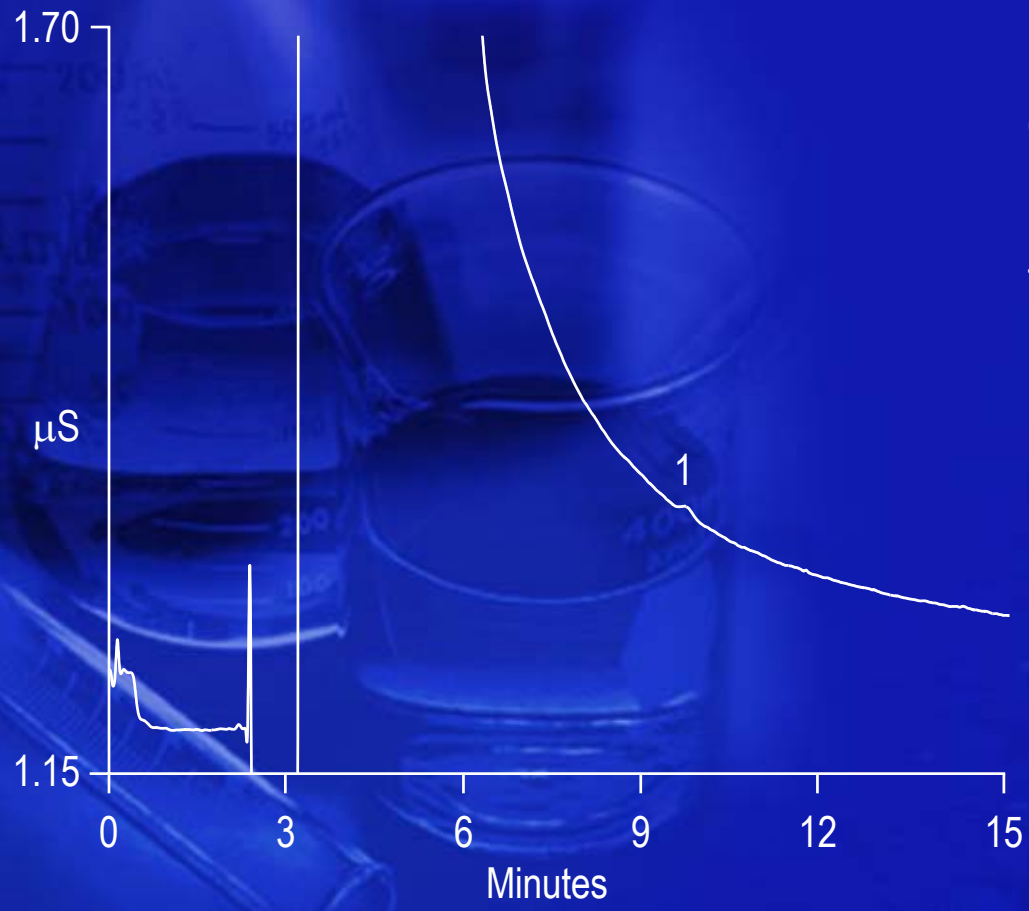
19866

Determination of 0.5 µg/L Perchlorate Spiked in Drinking Water



Instrument:	ICS 2000 RFIC
Columns:	IonPac® AG16, AS16, 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 with CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Inj. Volume:	1000 µL
Detection:	ASRS® ULTRA II, external water mode
Peaks:	1. Perchlorate 0.5 µg/L (ppb)

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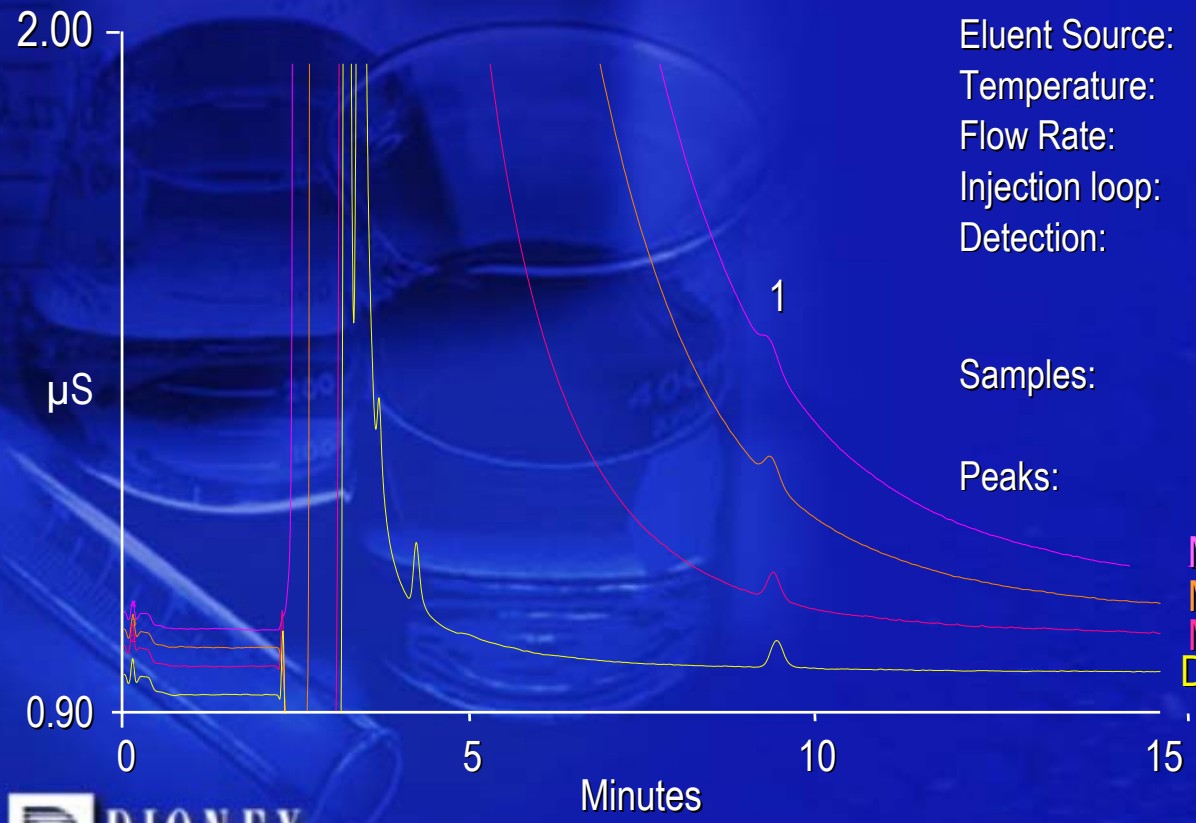
Reagent-Free IC

19500

EPA Method 314.0

Determination of 5 µg/L Perchlorate with Increasing Concentrations of Chloride, Sulfate, and Carbonate



Column:	IonPac® AG16, AS16, 4 mm
Eluent:	65 mM KOH
Eluent Source:	ICS-2000 EG with CR-ATC
Temperature:	30 °C
Flow Rate:	1.2 mL/min
Injection loop:	1000 µL
Detection:	ASRS® ULTRA II, AutoSuppression®, external water mode, 193 mA
Samples:	MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}
Peaks:	1. Perchlorate 5 µg/L

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19865

MDLs for Perchlorate on an ICS-2000

Matrix	MDL Standard (µg/L)	Retention Time RSD (%)	Calculated MDL[a] (µg/L)
DI water	0.5	0.10	0.10
50 (CCS)[b]	0.5	0.20	0.10
100 (CCS)	0.5	0.05	0.13
200 (CCS)	1.0	0.27	0.24
400 (CCS)	2.0	0.07	0.18
600 (CCS)	5.0	0.07	0.24

[a] The MDLs were calculated as MDL = (t) x (SD), n = 7

[b] CCS indicates a mixed common anion solution of chloride, carbonate and sulfate (mg/L each)

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OnGuard® Sample Pretreatment Removes Common Matrix Anions

$R–Ba + M,SO_4^{2-} \rightarrow R–M + BaSO_4 \downarrow$

$R–Ag + M,Cl^- \rightarrow R–M + AgCl \downarrow$

Removes AgCl colloids

$R–H + M, CO_3^{2-} \rightarrow R–M + H_2CO_3$

R = Resin
M = Metal Ions

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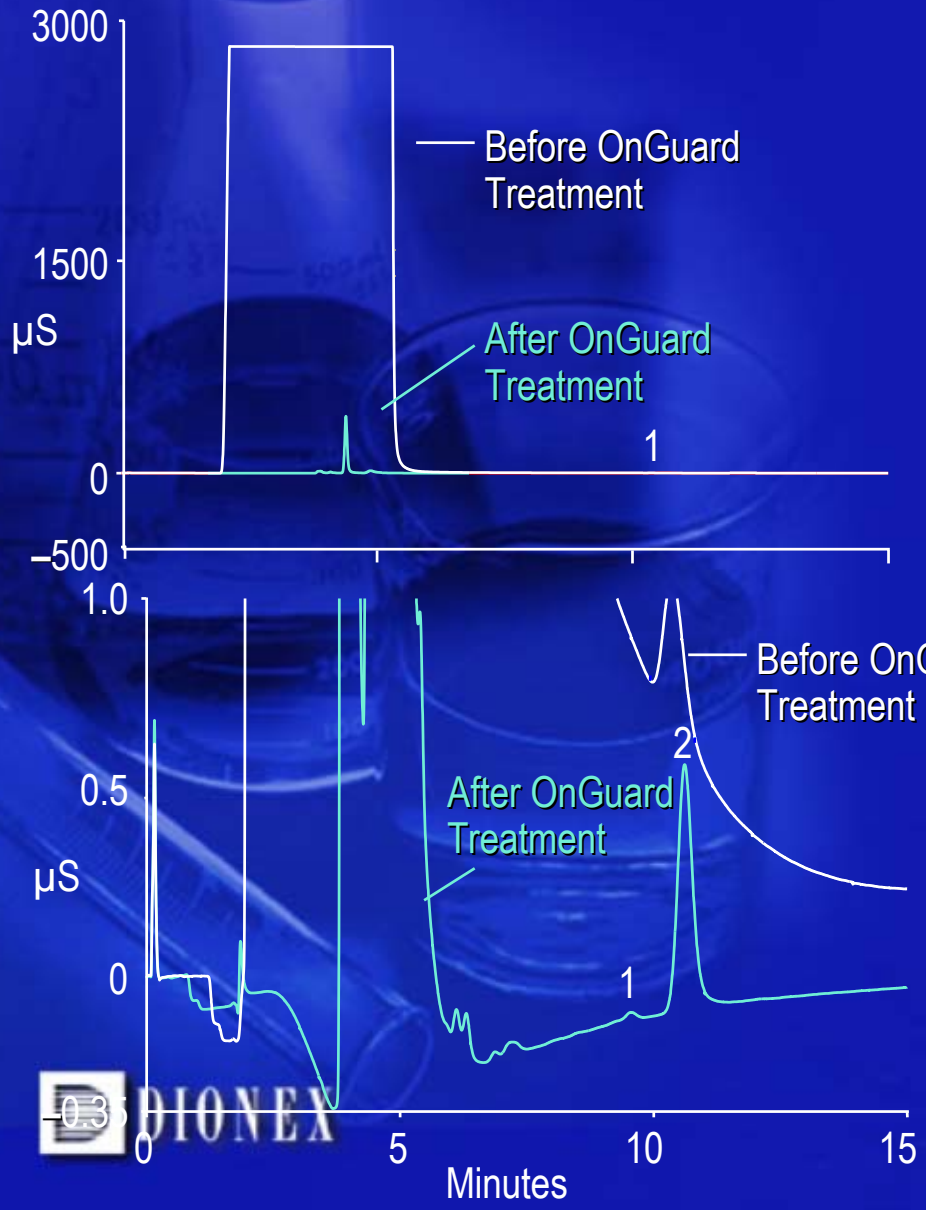
19152-modified

OnGuard® Matrix Elimination Improves Determination of Perchlorate in High-Ionic-Strength Water

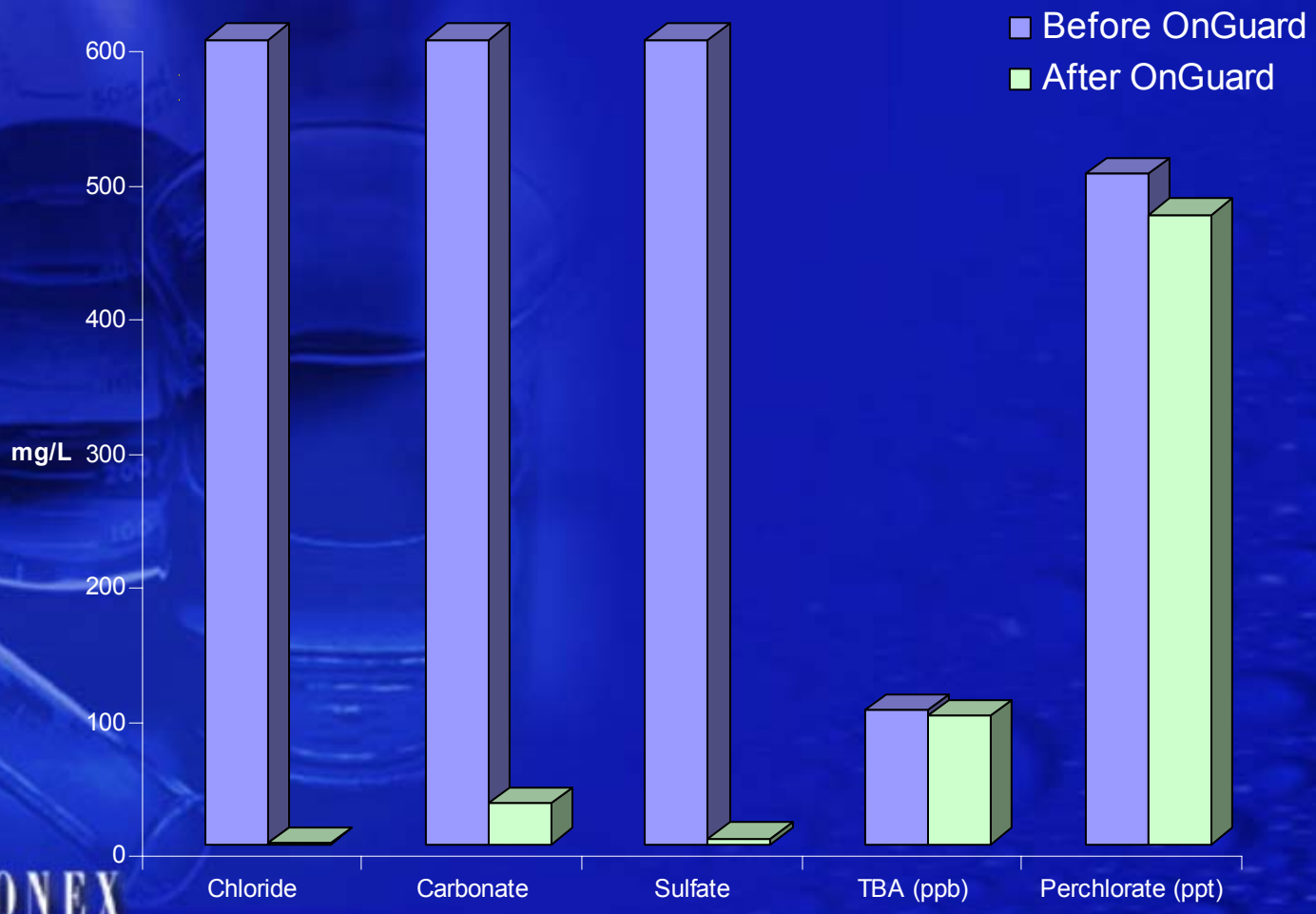


Column:	IonPac® AG16, AS16, 2 mm
Eluent:	50 mM potassium hydroxide (EG50)
Flow Rate:	0.4 mL/min
Inj. Volume:	1000 µL
Temperature:	30 ˚C
Detection:	Suppressed conductivity
Suppressor:	AMMS® III, 2 mm, pressurized bottle mode

Peaks:	1. Perchlorate	0.5	µg/L (ppb)
	2. Tribromoacetate	100	
Matrix:	Chloride	600	mg/L
	Carbonate	600	
	Sulfate	600	

19153-modified

OnGuard® Matrix Elimination of Chloride, Sulfate, and Carbonate Anions



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Precision of IC Determination of Perchlorate in a High TDS Sample Matrix[1] Using OnGuard® Matrix Elimination

Sample[(2)]	Perchlorate Concentration (µg/L)
1	0.388
2	0.318
3	0.319
4	0.347
5	0.336
6	0.283
7	0.321
Mean	0.330
SD	0.032
MDL[(3)]	0.100

1) Sample matrix contained chloride, carbonate, and sulfate at 600 mg/L each

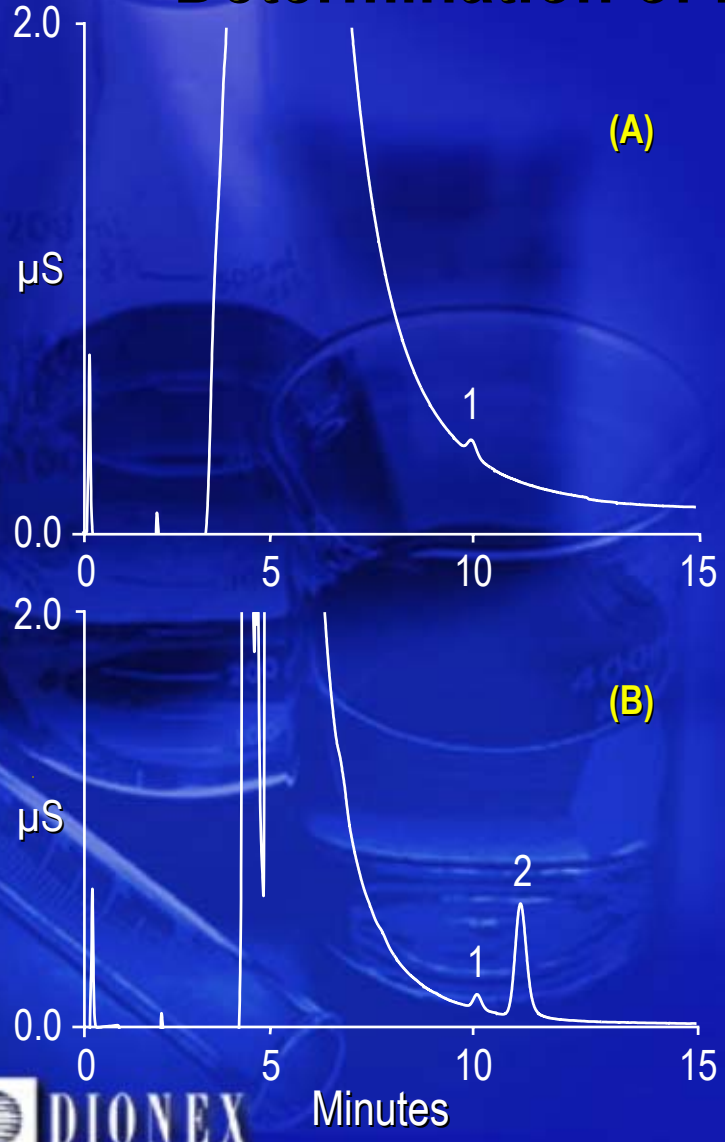
2) Each sample injected was treated with a different OnGuard cartridge set (Ba, Ag, filter,H)

3) MDL = method detection limit = (SD) x (t_s) 99% for 1 mL injection where (t_s) is for a 99% single-sided Students *t*-test for n = 7 which is 3.14

DIONEX

19156

OnGuard® Matrix Elimination Improves Determination of Perchlorate in Groundwater



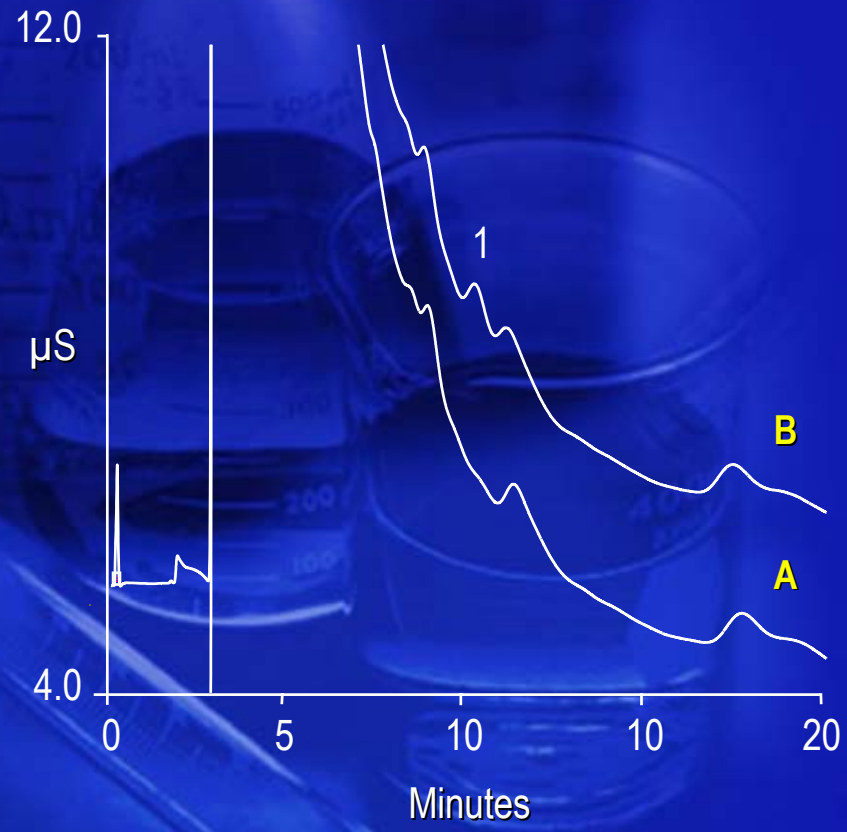
Column:	IonPac® AG16, AS16, 2 mm
Eluent:	50 mM potassium hydroxide (EG50)
Temperature:	30 °C
Flow Rate:	0.4 mL/min
Inj. Volume:	1000 µL
Detection:	Suppressed conductivity
Suppressor:	AMMS® III, 2 mm, pressurized bottle mode
Samples:	Domestic well water
	(A) No pretreatment
	(B) Pretreated with OnGuard Ba, Ag, H

		A	B	
Peaks:	1. Perchlorate	1.74	2.13	µg/L
	2. Tribromoacetate	–	86	

DIONEX

19491

OnGuard® Matrix Elimination Improves Recovery of Perchlorate Spike from Briny Surface Water



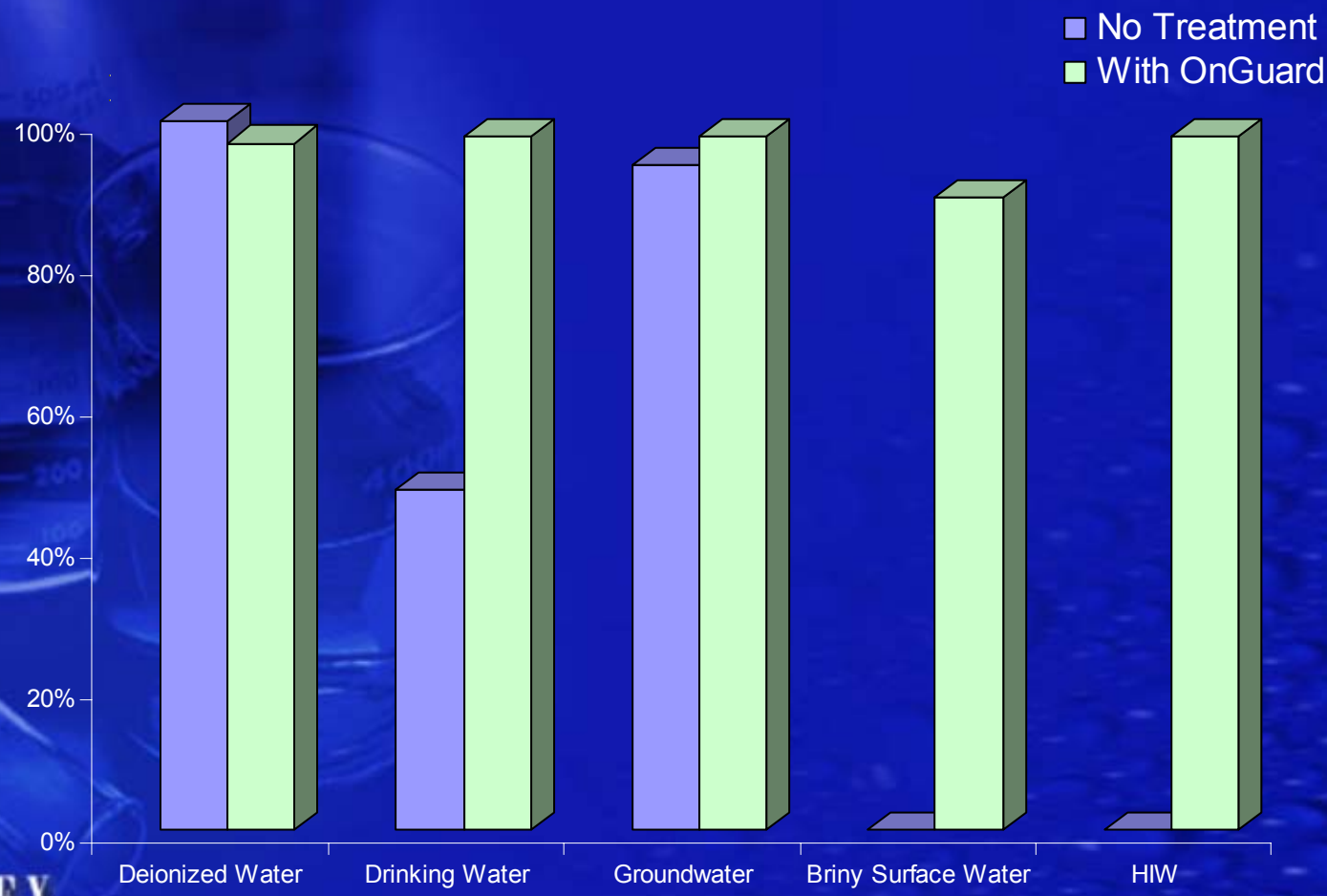
Column:	IonPac® AG16, AS16, 2 mm
Eluent:	65 mM potassium hydroxide (EG50)
Temperature:	30 °C
Flow Rate:	0.4 mL/min
Inj. Volume:	5 mL preconcentrated on TAC-ULPI
Detection:	Suppressed conductivity
Suppressor:	AMMS® III (2 mm) pressurized bottle mode
Sample:	Salton Sea surface water diluted 2x and pretreated with OnGuard Ba, Ag, H (A) Matrix blank (B) Matrix spiked with 5 µg/L perchlorate

			A	B	
Peaks:	1.	Perchlorate	n.d.	4.47	µg/L (ppb)

DIONEX

19495

OnGuard® Matrix Elimination Improves Recovery of Perchlorate Spiked Into Environmental Waters



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Conditions for Perchlorate Determination Using On-Line Sample Concentrator Column Technique

- **Method:** Ion chromatography with chemically suppresssed conductivity detection
- **Conditions:**
  - Column: IonPac® AG16, AS16, 2-mm set
  - Eluent: Sodium hydroxide (EG50)
  - Flow rate: 0.25 mL/min
  - Suppressor: ASRS ULTRA® II, recycle mode
- **Sample Loop:** Replace with Cryptand concentrator column.
- **Program:** Apply 5-mL of sample to concentrator column.
  Rinse with 1 mL of 10 mM sodium hydroxide.
  Elute with 0.5 mM sodium hydroxide for 12 min.
  Separate with 60 mM sodium hydroxide.

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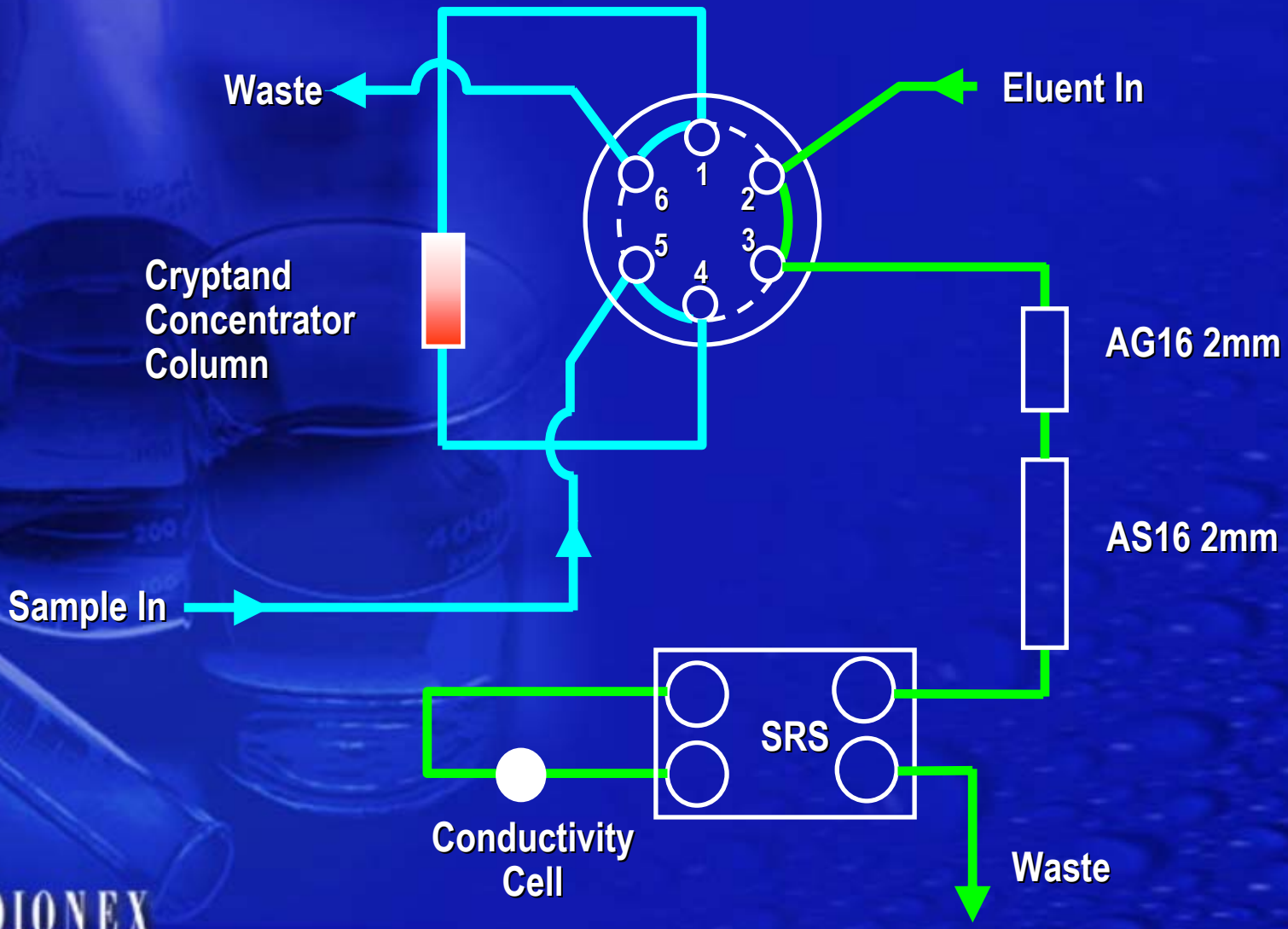
On-line Sample Sample Concentration Technique

Loading the Concentrator Column



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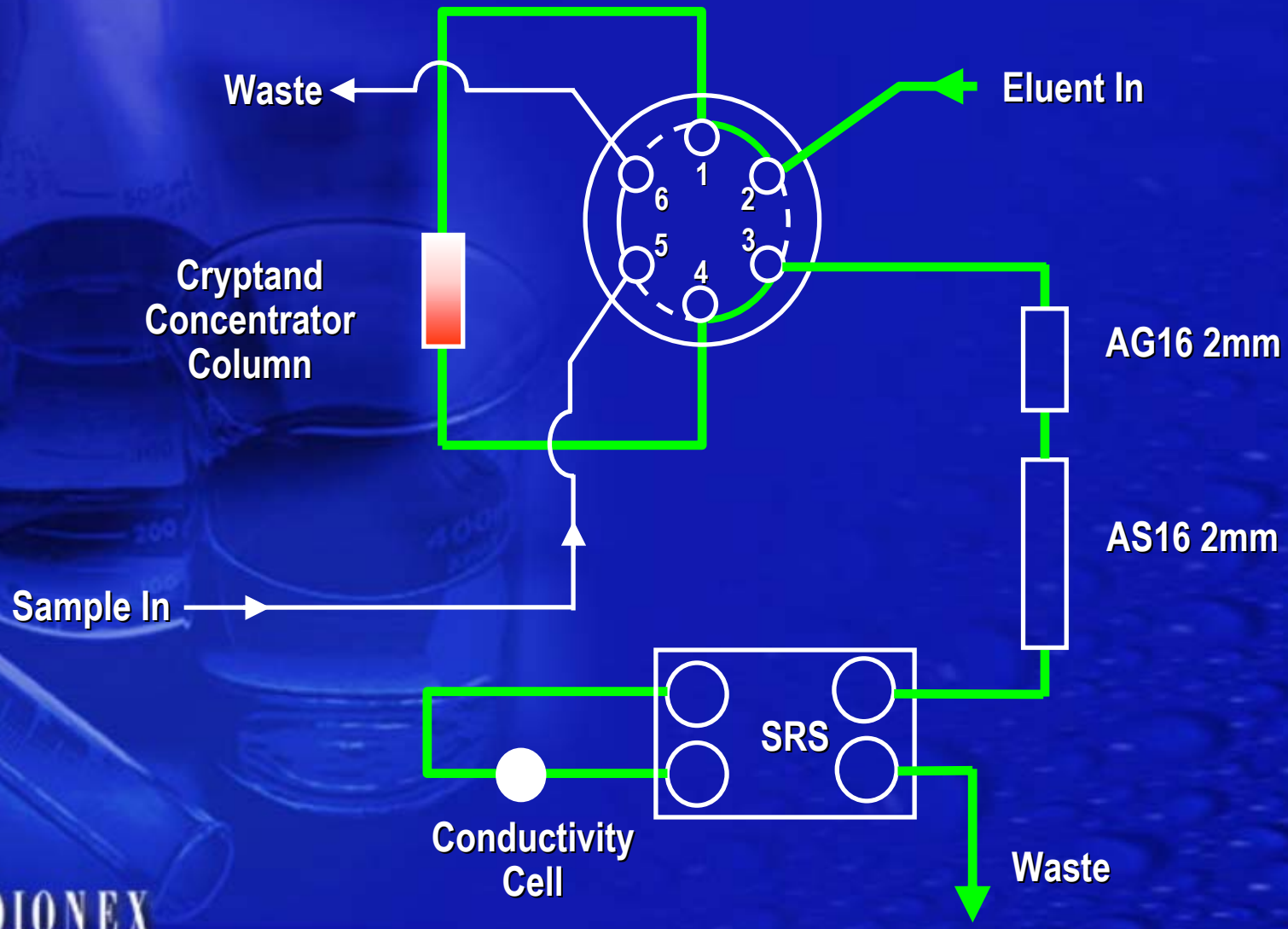
19868

On-Line Sample Concentration Technique

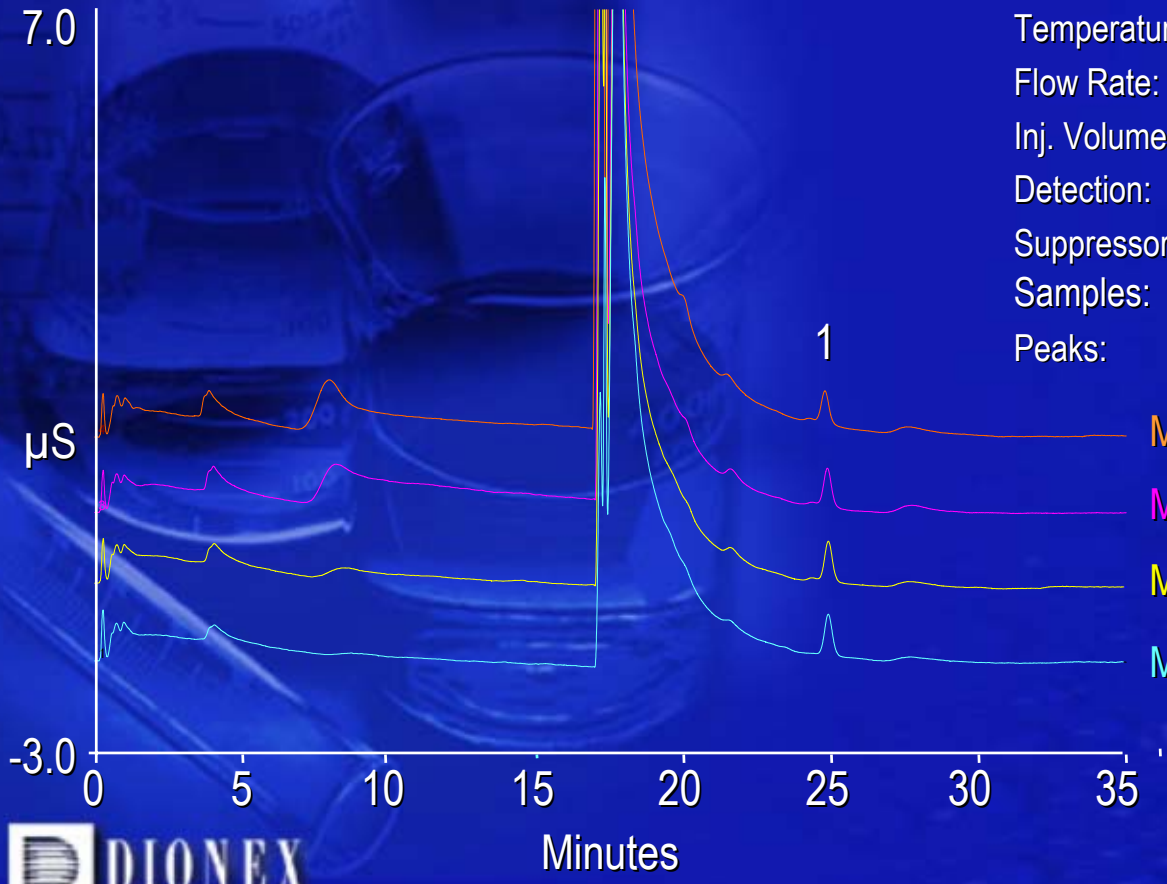
Separating the Concentrated Ions



DIONEX

19869

Recovery of Perchlorate Spike From High-Ionic-Strength Water Matrices



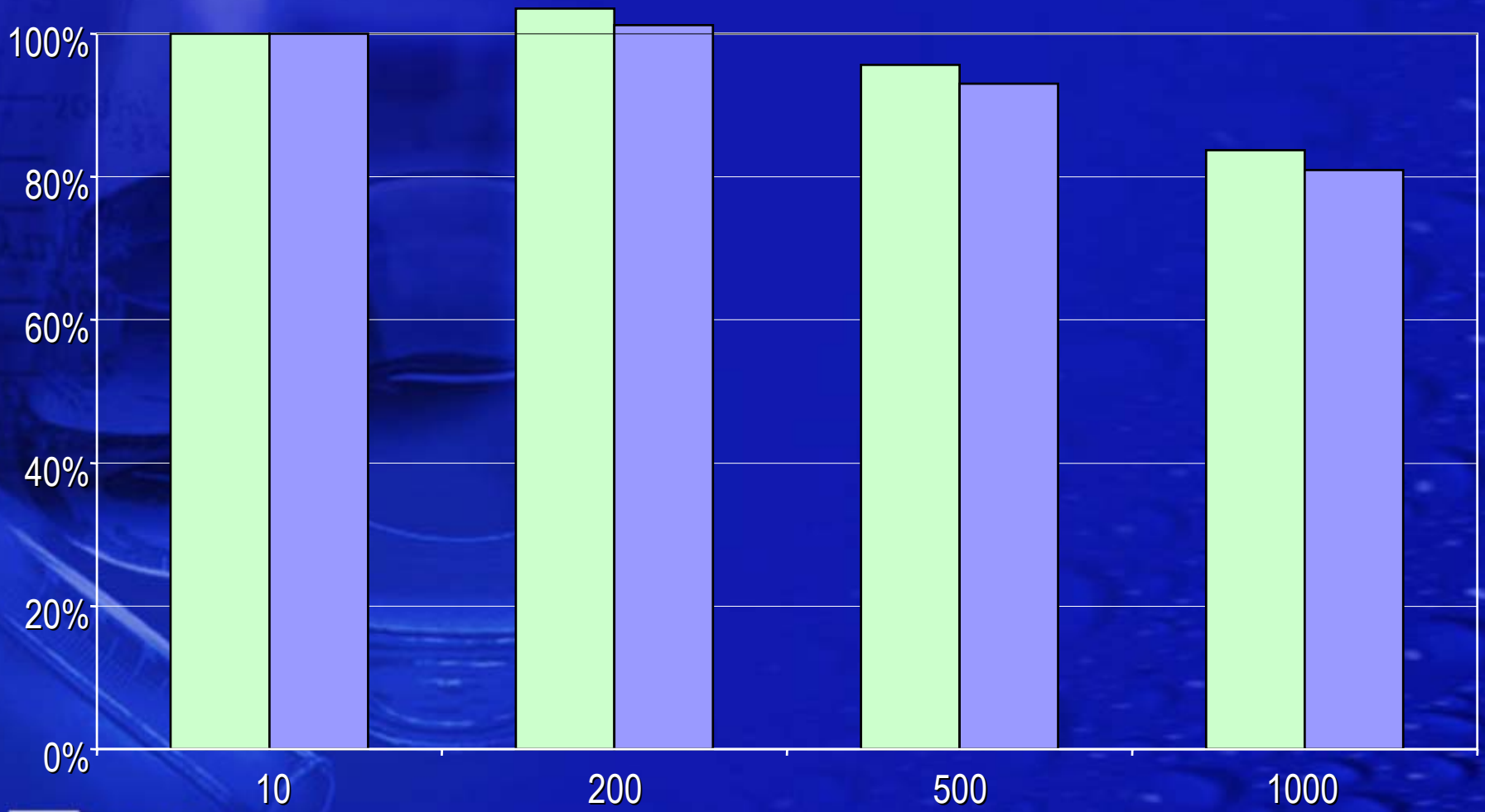
Column:	IonPac® AG16, AS16, 2 mm
Eluent:	60 mM potassium hydroxide (EG50)
Temperature:	30 °C
Flow Rate:	0.25 mL/min
Inj. Volume:	5 mL preconcentrated on 09-42C 4 x 35 mm
Detection:	Suppressed conductivity
Suppressor:	ASRS ULTRA® II 2 mm, recycle mode
Samples:	MA(x) = X mg/L each Cl^-, SO_4^{2-}, CO_3^{2-}
Peaks:	1.Perchlorate 2 µg/L

DIONEX

19867

Recovery of 2 ppb Perchlorate in HIW Matrices

Cryptand 09-42C 4 x 35 mm
5 mL concentrated with 1-mL of 10 mM NaOH rinse



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19870

Summary

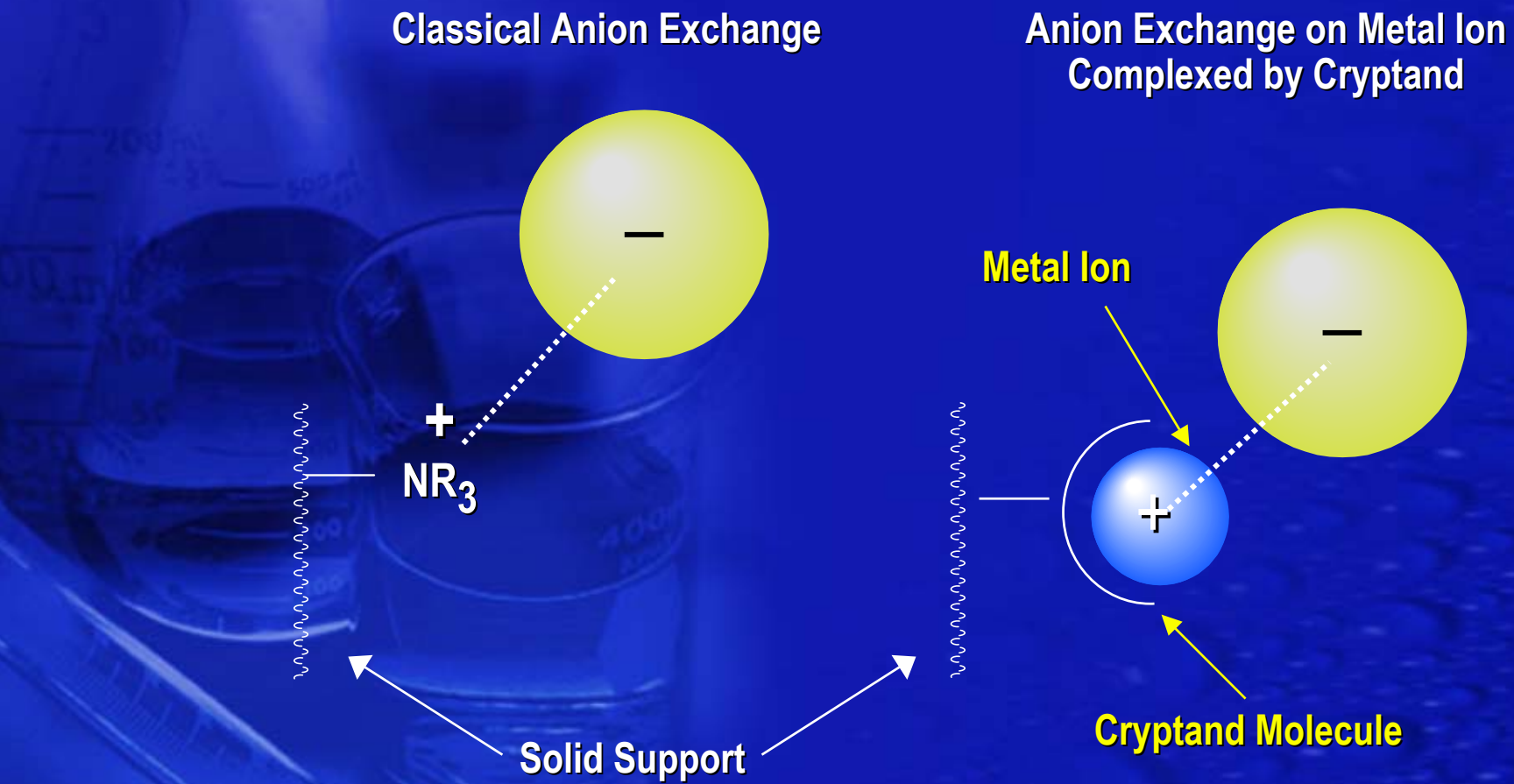
- Benefits of on-line sample concentration:
  - Up to 5x more perchlorate injected onto 2-mm AS16
  - Elution from Cryptand concentrator column with low-concentration eluent refocuses perchlorate onto AS16
  - Matrix ions significantly reduced in concentration allowing better sensitivity

Future work:

- Measure linearity of perchlorate peak area vs. concentration
- Find a suitable surrogate/internal standard

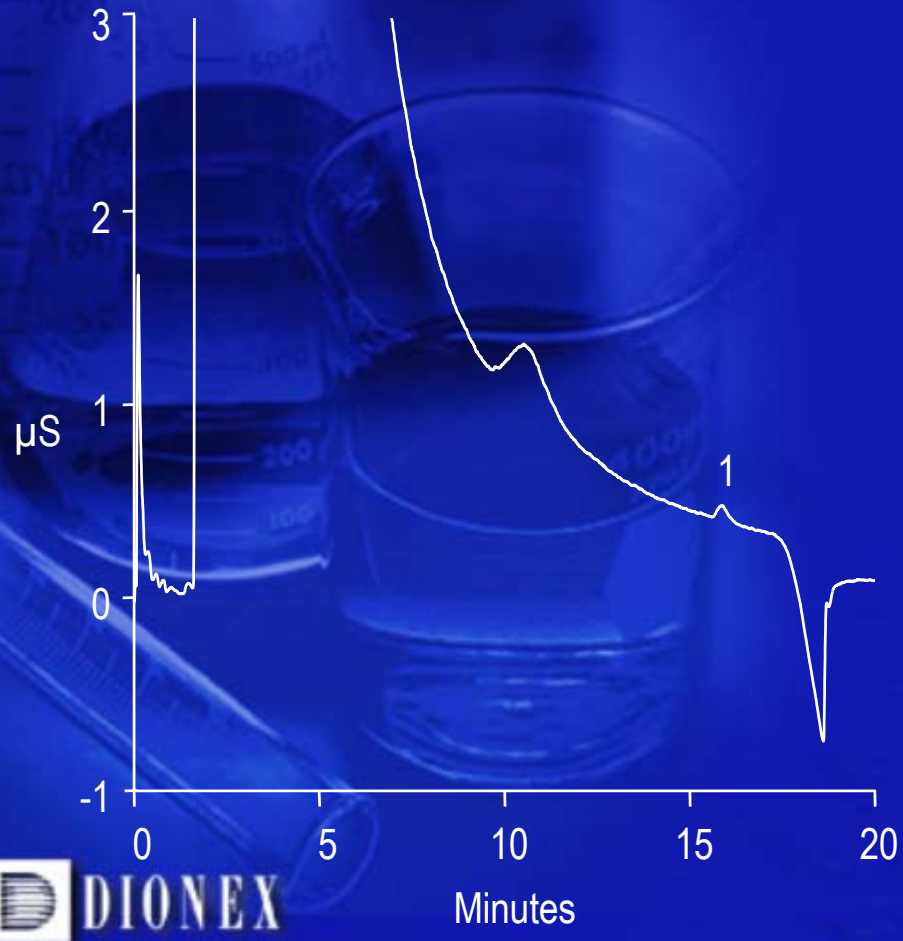
DIONEX

Comparison of a Classical IC Column and an IonPac® Cryptand Column



DIONEX

Determination of Perchlorate in High TDS Samples Using a Cryptand Column



Column:	IonPac® Cryptand A1, 5 µm, 3 x 150 mm
Eluent:	35 mM NaOH, step to 35 mM LiOH at 5 min., step back to 35 mM NaOH at 13 min.
Flow Rate:	0.5 mL/min
Inj. Volume:	1 mL
Temperature:	35 ˚C
Detection:	Suppressed conductivity ASRS® ULTRA, 2 mm, external water mode with ATC (4 x 35 mm)
Peaks:	1. Perchlorate 4 µg/L (ppb)
Sample:	DI Water with:

Chloride	800	mg/L
Carbonate	1000	
Sulfate	1200	

DIONEX

19157

Precision of Perchlorate Determination in a High TDS Sample Using a Cryptand Column

Injection	Perchlorate Concentration µg/L
1	1.81
2	1.94
3	2.32
4	1.88
5	2.16
6	2.06
7	1.83
Mean	2.00
SD	0.19
MDL	0.60
RSD	9.5%

Sample – DI water (1 mL injected) with:

Chloride	400	mg/L
Carbonate	600	mg/L
Sulfate	500	mg/L
Perchlorate	2	µg/L

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19158

RFIC-MS for Perchlorate

Benefits of Combining Suppressed IC with MS

ICS-2500

MSQ™

- Separate ionic analytes using standard IC conditions
- Suppressor permits use of high-ionic-strength eluents to get the benefits of high-capacity columns
- Detect and identify analytes with high specificity
  - Avoid coeluting interferences to ensure accurate identification
  - Avoid background interferences to ensure highest analyte sensitivity
  - Identify analytes by mass and isotope ratios for added confirmation
- Identify unknowns

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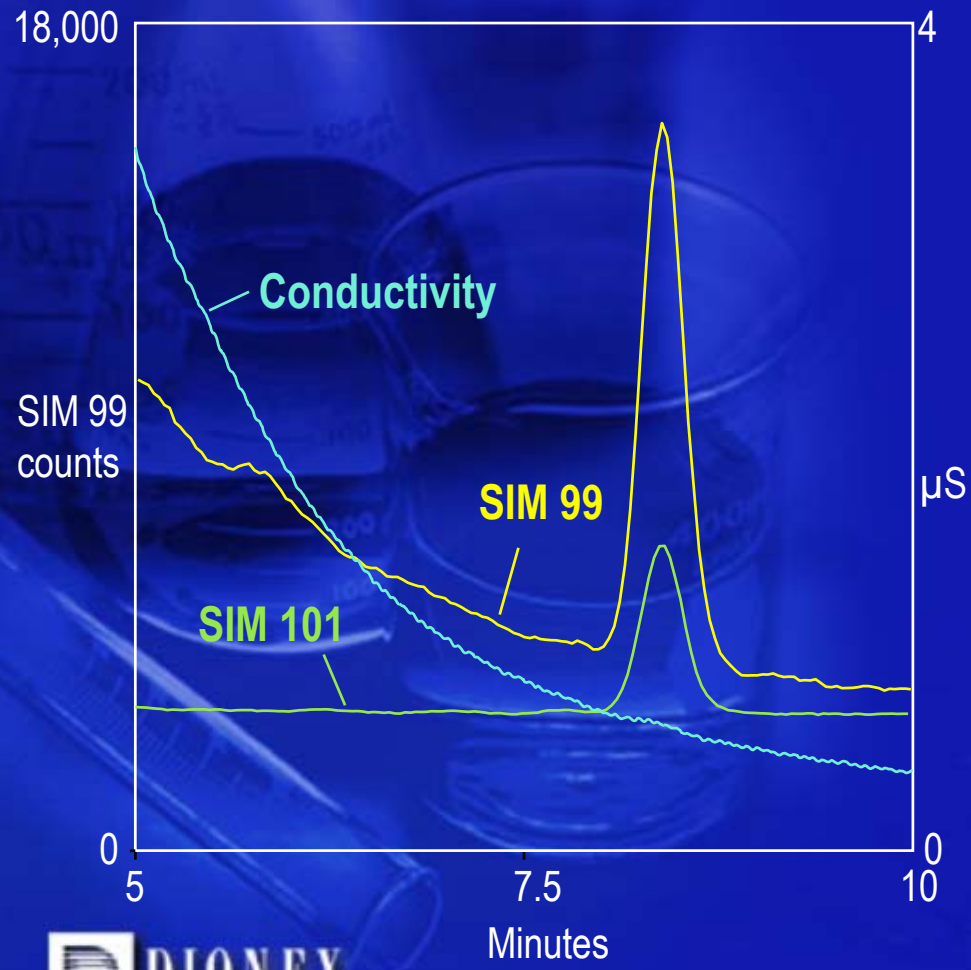
MSQ is a trademark of Thermo Electron Corp.

19740

RFIC-MD-MS of Perchlorate in California Groundwater



Column:	IonPac® AG16, AS16 (2-mm)
Suppressor:	ASRS® ULTRA, 2 mm
Eluent:	65 mM KOH (EG40)
Eluent source:	EGC-KOH with CR-ATC
Flow Rate:	0.30 mL/min
Inj. Volume:	250 µL
Detection:	1. Conductivity 2. MS, SIM 99, $^{35}ClO_4^-$ 3. MS, SIM 101, $^{37}ClO_4^-$
MS Conditions:	–ESI, 70 V, 350 °C
Sample:	Groundwater diluted 1/10
Peak:	Perchlorate ~ 7–8 µg/L

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19161

IC-MS Method Performance Enhancement Developments

- **Matrix Diversion**: *diverting the high concentration matrix ions, such as chloride, carbonate and sulfate, away from the MS using valve switching while they are eluting from the ion exchange column and then directing the column effluent to the MS while perchlorate elutes.*
- **Solvent Wash**: *rinsing the source cone with a solvent while the matrix ions are being diverted away from the MS; this provides continuous cleaning of the entrance oriface to the MS and enhances method performance*

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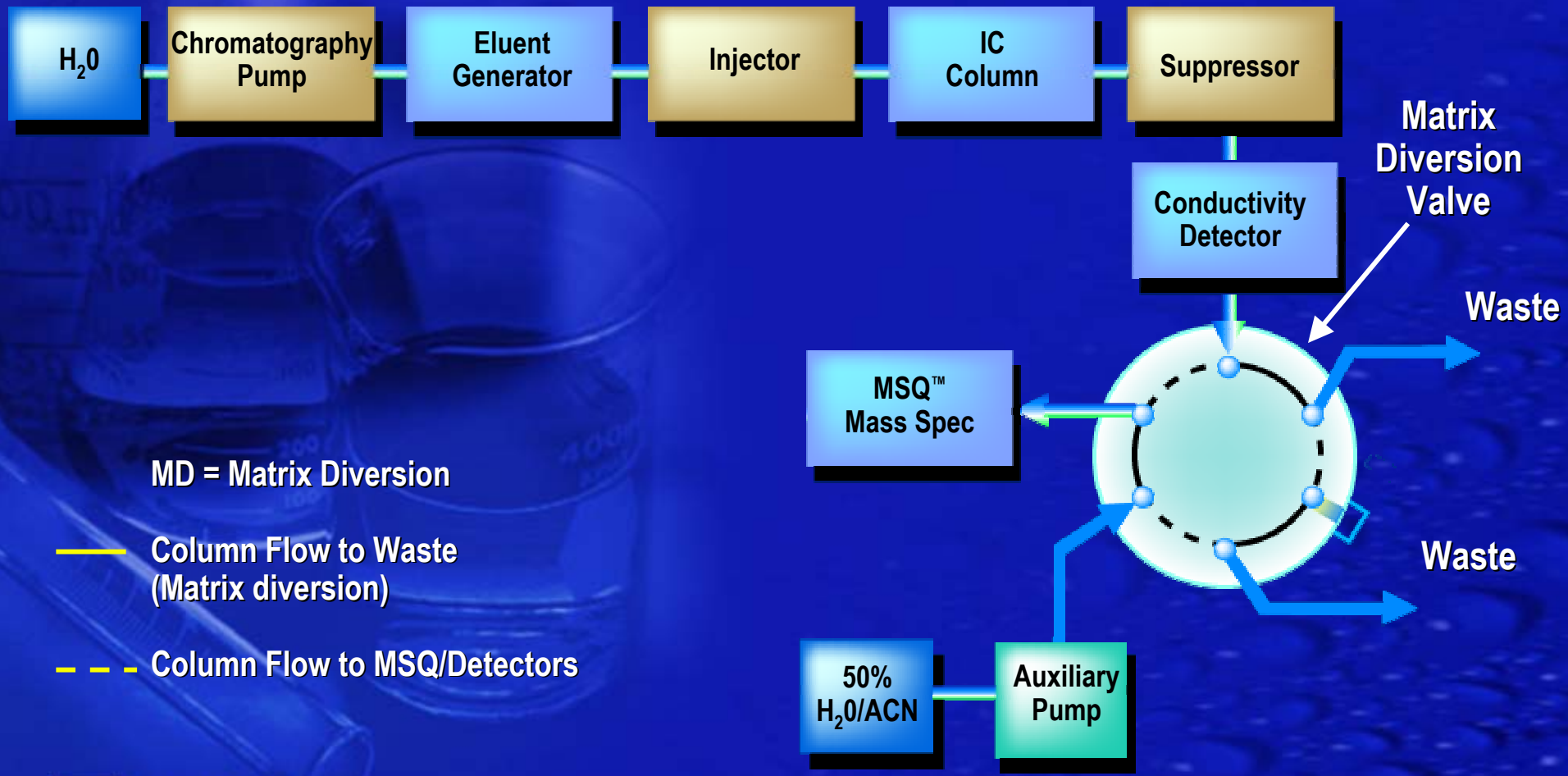
RFIC-MD-MS for Perchlorate



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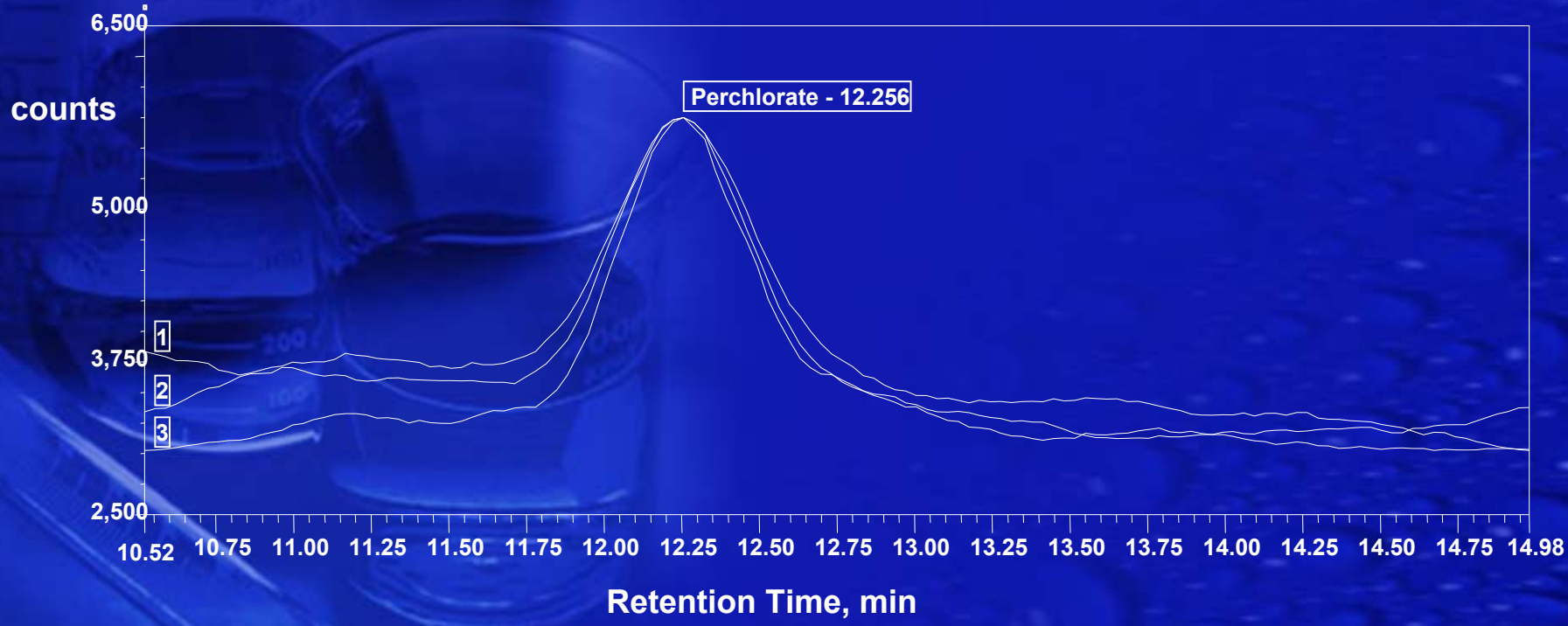
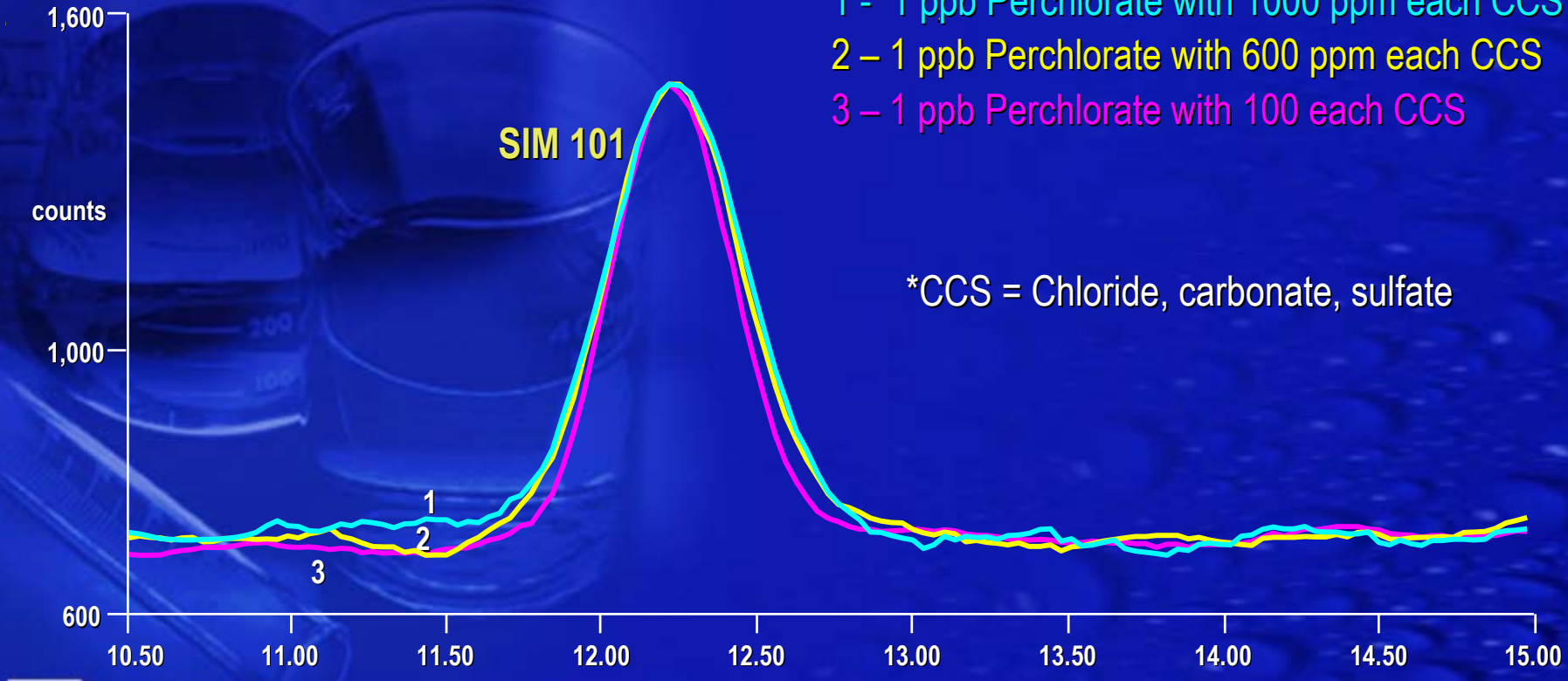
SIM 99 MS Response
Solvent Wash ME-IC-MS with 50% ACN

- 1 - 1 ppb Perchlorate with 1000 each CCS
- 2 – 1 ppb Perchlorate with 600 each CCS
- 3 – 1 ppb Perchlorate with 100 each CCS



DIONEX

Low-Level Perchlorate Analysis
RFIC-MD-MS with 50% ACN Solvent Wash



1 - 1 ppb Perchlorate with 1000 ppm each CCS
2 – 1 ppb Perchlorate with 600 ppm each CCS
3 – 1 ppb Perchlorate with 100 each CCS

*CCS = Chloride, carbonate, sulfate

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19741

Benefits of Matrix Diversion for the Analysis of Perchlorate by RFIC-MS

- Removal of early-eluting matrix ions
- High recovery regardless of matrix
- Isotopic chlorine ratio confirms perchlorate identification
- No prescreening of samples
- Eliminates off-line sample pretreatment (materials and labor)

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Precision and MDL Perchlorate in a High TDS Sample Matrix

	RFIC-OnGuard[2,4] (1 mL inj.)		RFIC-MD-MS[1] (250 µL inj.)
Injections	Concentration (µg/L)	Injections	Concentration (µg/L)
1	0.388	1	0.232
2	0.318	2	0.230
3	0.319	3	0.254
4	0.347	4	0.254
5	0.336	5	0.259
6	0.283	6	0.284
7	0.321	7	0.236
Mean	0.330	Mean	0.250
SD	0.032	SD	0.019
MDL[3]	0.100	MDL[3]	0.06

1 Sample matrix: 100 mg/L chloride, 300 mg/L carbonate, 400 mg/L sulfate

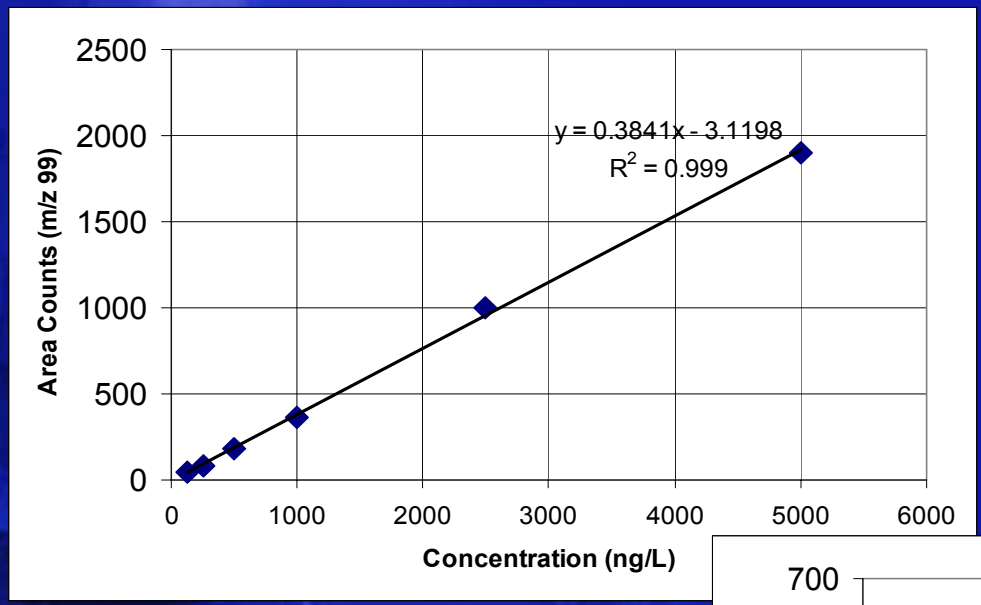
2 Sample matrix contained chloride, carbonate and sulfate at 600 mg/L each

3 MDL = method detection limit = (SD) + (t_s) 99% where (t_s) is a 99% single-sided Students *t* test for n = 7 which is 3.14

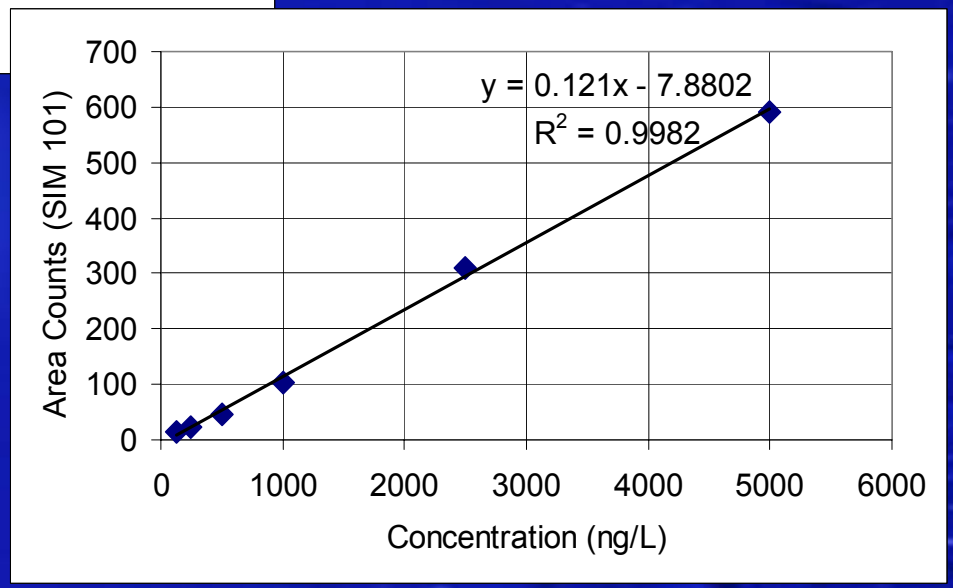
4 Each sample injected was treated with a different OnGuard cartridge set (Ba, Ag, filter, H)

DIONEX

Perchlorate Calibration Curves Drinking Water Matrix with IC-MD-MS



Mass 99 Calibration



Mass 101 Calibration

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Performance Enhancements Summary

Solvent Wash MD-IC-MS versus ME-IC-MS

- Water Wash MD-IC-MS MDL: 50-80 ppt
- Water as a Wash Solvent results in about a10% absolute improvement in area count stability
- ACN Solvent Wash MD-IC-MS MDL: 30-50 ppt
- 50% Acetonitrile as a Wash Solvent improves detection limits about 25%, day-to-day reproducibility an additional 10% in high ionic strength matrices, recovery up to 100% depending on background conductivity

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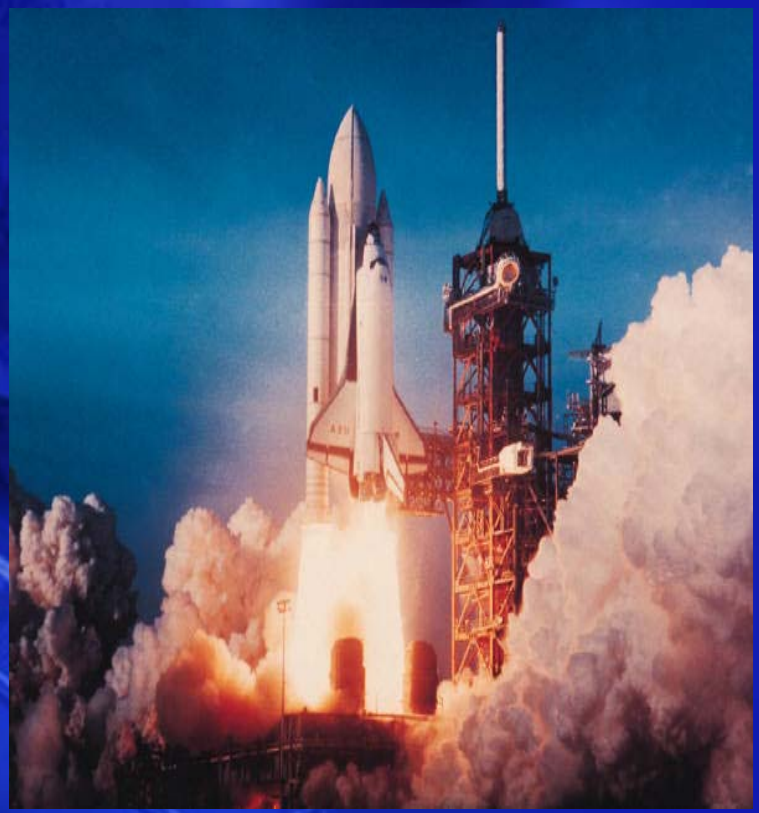
IC-MS/MS Collaborative Study
Preliminary Data

- Instrumentation:
  - DX-600 Ion Chromatograph with AS16 column and Ultra II suppressor
  - Micromass Quattro Ultima Tandem MS with collision cell monitoring the m/z 99 to 83 and 101 to 85 transitions
  - 83 m/z used for quantitation
- Calibration Range: 5 – 100 ng/L in reagent water
- MDL determination at 2 ng/L (ppt) results in an MDL of ~ 1ng/L
- Perchlorate estimated quantitation limit in ground water matrices at ~5-10 ng/L

DIONEX

Summary

Determination of Perchlorate in Drinking Water Using Ion Chromatography



- 0.5 – 1.0 µg/L with Suppressed Conductivity
- <100 ng/L with Standard Suppressed IC-MS
- <50 ng/L with Suppressed Solvent Wash ME-IC-MS
- <5 ng/L with Suppressed IC-MS/MS
- IC-MS Delivers Superior Sensitivity and Selectivity

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